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(54)【発明の名称】 多孔質セラミックス膜とその製造方法

(57)【要約】

【課題】 分子や微粒子を分離するために好適に使用される、圧力損失の少ない一次元貫通気孔を有する様々な組成のセラミックスフィルタを提供する。

【解決手段】 膜の一方の表面からもう一方の表面に一次元的に貫通するナノメートルサイズの気孔を有する多孔質セラミックス膜であって、多孔質セラミックス膜がガラス、セラミックス、プラスチック又は耐熱金属の基板上に形成されていることを特徴とする多孔質セラミックス膜。さらに、気相成長法によって基板上にセラミックス相と金属相からなる複合膜を形成し、次いで複合膜中の金属相をエッチングで除去することを特徴とする膜の一方の表面からもう一方の表面に一次元的に貫通するナノメートルサイズの気孔を有する多孔質セラミックス膜の製造方法。

【効果】 ナノメートルオーダーの細孔径の一次元貫通孔を有する多孔質セラミックス膜を再現性良く合成することが可能となる。また、様々な基板上に形成することによって、ナノメートルサイズでの分離機能を発現させることができる。

【特許請求の範囲】

【請求項1】 気相成長法によって成膜したセラミックス相と金属相からなる複合膜中の金属相を除去して得られる、膜の一方の表面からもう一方の表面に一次元的に貫通するナノメーターサイズの気孔を有する多孔質セラミックス膜であって、当該多孔質セラミックス膜がガラス、セラミックス、プラスチック又は耐熱金属の基板上に形成されていることを特徴とする多孔質セラミックス膜。

【請求項2】 前記多孔質セラミックス膜が金属酸化物、金属炭化物及び金属ホウ化物から選ばれる一種以上の化合物である請求項1記載の多孔質セラミックス膜。

【請求項3】 前記多孔質セラミックス膜を支持する基板が多孔質体である請求項1又は2記載の多孔質セラミックス膜。

【請求項4】 前記一次元的に貫通する気孔の平均孔径が5〜100ナノメートルである請求項1記載の多孔質セラミックス膜。

【請求項5】 気相成長法によって基板上にセラミックス相と金属相からなる複合膜を形成し、次いで複合膜中の金属相をエッチングで除去することを特徴とする膜の一方の表面からもう一方の表面に一次元的に貫通するナノメーターサイズの気孔を有する多孔質セラミックス膜の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、多孔質セラミックス膜とその製造方法に関する。さらに詳しくは、本発明は、分子や微粒子を分離するために好適に使用される、圧力損失の少ない一次元貫通気孔を有する様々な組成の多孔質セラミックス膜と当該多孔質セラミックス膜を再現性良く製造する方法に関する。本発明の多孔質セラミックス膜は、ナノメーターサイズでの分離機能を発現することから、各種の分子や微粒子の分離手段等として有用である。

【0002】

【従来の技術】高温のガスや腐食性の液体中に含まれる分子や微粒子を分離することを目的とする耐熱性と耐食性に優れたセラミックスフィルタが開発されている。多孔質セラミックス体もしくは多孔質セラミックス膜を製作する方法としては、セラミックス原料粉体を焼結し、セラミックス体が緻密化する過程で形成される開放気孔（セラミックス体の表面に開口する連通気孔）をそのまま利用する方法が多く採用されている（特開7-8729号公報）。しかしながら、このようにして作製したセラミックス体やセラミックス膜では細孔径のサイズを揃えることが難しく、かつナノメーターオーダーの細孔を再現性良く作製するのが難しいという問題があった。

【0003】ナノメーターオーダーの揃った細孔径を有する多孔体を再現性良く作製する試みとして、ゾル・ゲ

ル法とスピノーダル分解を組み合わせた手法で多孔質シリカが作製されている（Nakanishi et al., "Ceramic Transactions, Porous Materials", The American Ceramics Society, 51-60 (1992)）、この場合にはシリカ相が網目状に繋がった組織が形成され、細孔の形状は不規則でその方向はランダムである。

【0004】このように、細孔の形状が不規則でその方向が無配向であること、濾過方向に移動する分子や粒子を散乱して移動を妨げるセラミックス部分が多く存在することから圧力損失が発生する問題があった。

【0005】上記の問題を解決するため、細孔径がナノメーターサイズで、しかも、一次元的に貫通する細孔（以下、一次元貫通気孔ということがある）を有するセラミックス膜の開発が試みられている。その代表的な例として、アルミニウムの陽極酸化による多孔質アルミナ膜がある（特公平6-37291号公報）。アルミニウムの陽極酸化で作製された膜は、その作製条件によって細孔径が数ナノメーターから数十ナノメーターの範囲で制御でき、また膜の組成がアルミナであるため、相当の耐熱性と耐食性が期待できるという利点がある。しかし、陽極酸化による多孔質アルミナ膜の場合、金属アルミニウム箔や厚さのあるアルミニウム板の電解液中での陽極酸化を利用するという原理上の制約から、得られる膜が常温付近でのみ安定な無定形のアルミナに限られ、また、基板としてアルミニウム板しか選べないという欠点がある。

【0006】上記陽極酸化による多孔質アルミナ膜の欠点を補う方法として、陽極酸化で作製した多孔質アルミナ膜を鋳型として用い、ポリマーメンブレンに細孔パターンを転写する方法が試みられている（益田ら；日本セラミックス協会、1995年春季年会予稿、p4853F401）。しかし、この場合には陽極酸化による多孔質アルミナ膜の構造を転写する材料が有機物に限られており、また膜構造を転写したメンブレンを他の基板上に密着させて新たな複合膜とするのが難しいという欠点がある。

【0007】

【発明が解決しようとする課題】本発明の目的は、従来技術が有する前述の欠点を解消し、ガス分離膜や触媒に利用可能なナノメーターサイズの一次元貫通気孔を持つ多孔質セラミックス膜を多様なセラミックス材料（金属酸化物、金属炭化物又は金属ホウ化物等）で提供することにある。さらに、各種の多孔質セラミックス膜をガラス、セラミックス、プラスチックあるいは耐熱金属からなる緻密質又は多孔質の基板上に形成した新規な複合膜を提供すること、このようなセラミックス膜を再現性良く製造する方法を提供することにある。

【0008】

【課題を解決するための手段】本発明は、前記の課題を解決すべくなされたものであり、本発明の多孔質セラミ

ックス膜は、気相成長法によって成膜したセラミックス相と金属相からなる複合膜中の金属相を除去して得られる、膜の一方の表面からもう一方の表面に一次元的に貫通するナノメーターサイズの気孔を有する多孔質セラミックス膜であって、当該多孔質セラミックス膜がガラス、セラミックス、プラスチック又は耐熱金属の基板の上に形成されていることを特徴とする。本発明による好ましい多孔質セラミックス膜は、前記の多孔質セラミックス膜を構成する物質が金属酸化物、金属炭化物及び金属ホウ化物から選ばれた少なくとも一種の化合物である。本発明の他の好ましい多孔質セラミックス膜は、前記多孔質セラミックス膜を支持する基板が多孔質体である。本発明の他の好ましい多孔質セラミックス膜は、前記一次元的に貫通する気孔の平均孔径が5~100ナノメートルである。本発明の多孔質セラミックス膜の製造方法は、気相成長法によって基板上にセラミックス相と金属相とからなる複合膜を形成し、次いで複合膜中の金属相をエッチングで除去することと特徴とする。

【0009】

【発明の実施の形態】 続いて、本発明についてさらに詳細に説明する。すなわち、本発明の多孔質セラミックス膜は二段階のプロセスで作製される。第一段階ではスパッタ法などの気相成長法を用いて金属とセラミックス材料（金属酸化物、金属炭化物あるいは金属ホウ化物）がナノメータースケールで混在した膜を作製する。このとき、用いる金属相とセラミックス材料の混合比及び成膜条件を制御することにより柱状に成長した金属相のみをセラミックス材料が取り囲んだ微細組織が形成される（図1）。本発明においては、金属相の粒径により孔径を変化させることが可能である。この場合、金属相の平均粒径は金属相とセラミックス相の体積分率及び成膜条件（基板温度、スパッタ時の残留ガス圧力等）により、およそ5~500nmの範囲で変えることができる。また、セラミックスフィラー部分として残存する粒界相の厚みは金属相とセラミックス相の体積分率で変化させることができる。従って、膜を作製する場合のパラメーターとして膜組成と成膜条件を独立に変えることが可能であり、粒界相の平均の厚みはおよそ1~50nm程度で変化させることができる。図1において暗く見える部分がC₀結晶粒であり、白い網目状の部分がC₀結晶粒の粒界に析出したSiO₂の部分である。C₀結晶粒の平均粒径は約12nm、SiO₂粒界層の幅は約2nmである。これと類似の膜構造は、例えば、ハード磁気ディスクの酸化物でC₀-Pt系合金とSiO₂の混合系で実現している（特願平7-51410号）。引き続き、第二段階で酸あるいはアルカリを用いて金属部分を除去することにより最終的に一次元の貫通気孔を有する多孔質セラミックス膜が得られる。本発明の多孔質セラミックス膜は多孔質セラミックス基板上に形成する手順の概略図を図2に示す。図中、（a）は多孔質セラ

ミックス基板の断面図、（b）はセラミックス基板上に金属膜を形成した状況（基板表面の細孔は金属で充填される）、（c）はセラミックス基板表面が現れるまで表面を研磨した状態、（d）は（c）で得られた膜の上に本発明の金属・セラミックス複合膜を形成した状態、（e）は酸によるエッチングで金属を溶出した後の状態、をそれぞれ示す。

【0010】第一段階で用いられる気相成長法としては、スパッタ法、蒸着法、CVD法、レーザーアブレーション法あるいは分子線エピタキシー法などが考えられるが、量産性や大面積成膜の可能性を考慮してスパッタ法を用いることが好ましい。

【0011】金属とセラミックス材料の組み合わせとしては、金属とセラミックス材料が成膜時に相分離を起こす組み合わせであれば良い。本発明においては、柱状に成長する金属相をエッチング後の細孔部分に、柱状に成長した金属相の粒界部分に析出したセラミックス相を残留相として利用するため、金属相としては柱状に成長し易い金属であって、酸・アルカリに容易に溶解し、酸素、炭素、ホウ素との結合エネルギーが小さく還元され易い金属又は合金が好ましい。実用的にはスパッタ時の取り扱いの容易さを考慮し、V、Cr、Mn、Ni、Fe、Co、Cu、Znなどの3d遷移金属及びそれらを主成分とする合金、Mgなどのアルカリ土類金属及びそれを主成分とする合金から選ばれる一種以上が好適である。その他、Al、In、Sn及びPbなどが利用可能である。残留相として利用するセラミックス相としては、アルミナ、ムライト、コーディエライト、スピネル、ゼオライト、フッ素セライトなどの酸化物、炭化ケイ素、炭化チタン、炭化ジルコニウムなどの炭化物、ホウ化チタン、ホウ化ジルコニウム、炭化ホウ素などのホウ化物から選ばれる一種以上が好適に利用できる。

【0012】スパッタ法等によって上記金属とセラミックスの複合膜を成膜する場合、金属のターゲットの上に金属酸化物、金属炭化物、金属ホウ化物などのセラミックス材料の薄片を置き複合ターゲットとして用いることができる。さらに好ましくは、成膜後の膜内部での組成のばらつきを小さくするため、ターゲット作製時に粉末冶金的方法によって均一に混合した複合材料を用意する。

【0013】上述のような多孔質セラミックス膜を製造する際に用いる基板は、ガラス、セラミックス、プラスチック及び耐熱金属から選ぶことができ、さらに緻密な基板でなく多孔質の基板を用いることも可能である。基板に用いる耐熱金属としては、Fe、Ni、Cr、Vなどからなるステンレスやハステロイなどの耐酸化性の合金が好適である。図2は、一例として、多孔質セラミックス基板を用いて成膜する方法を示したものである。すなわち、平均孔径数ナノメーターから数十ミクロンメートルのセラミックス多孔体の表面に金属あるいは樹脂

を含浸した状態でその表面を研磨し、平滑な表面を形成する。次いで、この表面を水、界面活性剤、有機溶媒等を用いて洗浄し、これを基板上としてその上にスパッタ膜を形成する。このとき、含浸する金属あるいは樹脂としては上記金属ターゲットの材料と同一のエッチング条件で取り除けるものを使用するのが好ましい。

【0014】次に、得られた複合膜中の金属成分を酸又はアルカリ溶液でエッチング処理して取り除く。このエッチング処理で用いる酸としては、硫酸、塩酸、硝酸、シュウ酸、酢酸などを用いることができ、溶出すべき金属の種類によって適宜選ぶことが好ましい。最初の成膜プロセスによって形成されるセラミックス部分はアモルファスあるいは結晶化の程度の低いものが多いため、十分に希釈された溶液を用いて弱いエッチング条件でエッチングすることが好ましい。例えば、金属成分としてCoを用い、セラミックス成分としてSiO₂を用いる場合、0.003規定の硝酸水溶液を用い、毎秒0.3ナノメートルのエッチング速度で処理することが好ましい。

【0015】以上述べたように、本発明の多孔質セラミックス膜の製造方法は、多孔質セラミックス膜を形成する際に金属とセラミックスの複合膜を気相成長法で作製し、次いでエッチングによって金属相を除去する方法を組み合わせて用いることを特徴としており、新規な構造と組成を有する種々の多孔質セラミックス膜を提供しうるものである。本発明の多孔質セラミックス膜は、ナノメートルサイズでの分離機能を発現させることが可能であり、分子や微粒子を分離するためのフィルターなどとして有用である。本発明の多孔質セラミックス膜は、細孔径と粒界幅の幅を独立に制御すること（特に、粒界幅の幅を厚くすること）が可能であり、この点で、従来の陽極酸化アルミナ膜などと本質的に異なるものである。

【0016】

【作用】本発明では、スパッタ法などの成膜法により、金属とセラミックス（金属酸化物、金属ホウ化物、金属炭化物）からなる化学的耐久性の異なる二相がナノメートルオーダーで混在する複合膜を形成し、次いで酸エッチング等により金属部分のみを取り除いてセラミックス部分を残留せしめることにより、圧力損失の少ない一次元貫通気孔を有する多孔質セラミックス膜を合成することが可能となる。すなわち、成膜条件を適切に制御することによって主要な膜成分の一つである金属相を柱状に成長させ、その粒界にセラミックス材料を析出させ、さらに金属相をエッチングで除くことによってナノメートルオーダーの細孔径の一次元貫通気孔を有する多孔質セラミックス膜を得ることが可能となる。

【0017】また、酸エッチングする前の複合膜はスパッタ法等によって形成するため、膜を支持する基板には金属、ガラス、セラミックス、プラスチックなど多種、多様な材料と形態のものが利用可能となる。

【0018】

【実施例】以下に本発明を実施例によって具体的に説明する。

実施例1

厚さ1.2mmのソーダライムガラス基板上に金属CoとSiO₂の2相からなる複合薄膜を形成した。スパッタには、直径6インチの金属Coターゲット上に1cm角のSiO₂ガラスチップを置いた複合ターゲットを用いた。このとき、ターゲットの片面の全表面積のうち20%を占めるようにSiO₂ガラスチップの量を調節した。真空槽を5×10⁻⁶Torrまで排気したのちにArガスを導入し、真空槽内部のガス圧が2×10⁻²TorrとなるようにArガスの流量を調節し、600Wの高周波を入力してプラズマを発生させた。このときの成膜速度はおよそ1nm/sであり、成膜時には基板加熱やバイアス電圧の印加は行わなかった。

【0019】成膜した複合薄膜の構造を図1の透過型電子顕微鏡写真に示す。図1はガラス基板を研削して取り除き、さらに複合膜をイオン研磨して薄くし、断面に垂直な方向から見た拡大写真である。この写真では、平均粒径12nmのCo結晶粒子が柱状に成長しており、粒界にアモルファスにSiO₂が析出している。

【0020】次に、上記の方法で作製した膜厚50nmの複合膜を0.003規定の硝酸水溶液に5分間浸漬してCo相を溶解除去した。図3はこのCo相を溶解除去した後の膜を走査型電子顕微鏡で観察した拡大写真である。Co相がほぼ完全に溶出し、粒界のSiO₂がメッシュ状に残留していた。図4にこのようにして得られたセラミックス膜の拡大、斜視図の一例を示す。

【0021】実施例2

実施例1と同様の手順で、厚さ1.2mmのソーダライムガラス基板上に金属CoとSiO₂の2相からなる複合薄膜を形成した。スパッタには、直径6インチの金属Coターゲット上に1cm角のSiO₂ガラスチップを置いた複合ターゲットを用いた。このとき、ターゲットの片面の全表面積のうち10%を占めるようにSiO₂ガラスチップの量を調節した。真空槽を5×10⁻⁶Torrまで排気したのちにArガスを導入し、真空槽内部のガス圧が2×10⁻²TorrになるようにArガスの流量を調節し、600Wの高周波を入力してプラズマを発生させた。このときの成膜速度はおよそ1nm/sであり、成膜時には基板の加熱やバイアス電圧の印加は行わなかった。

【0022】成膜した複合薄膜の構造は図1と非常に良く似たものであり、Coの結晶粒子が柱状に成長し、その粒界にアモルファスのSiO₂が析出しており、この場合にはCo結晶の平均粒子径は約20nmと若干大きくなった。この膜厚50nmの複合膜を0.003規定の硝酸水溶液に5分間浸漬してCo相を溶解除去した。実施例1の場合と同様に、Co相がほぼ完全に溶出

し、粒界の SiO_2 がメッシュ状に残留していた。

【0023】実施例3

実施例1と同様の手順で、厚さ1.2mmのソーダライムガラス基板上に金属Coと SiO_2 の2相からなる複合薄膜を形成した。スパッタには、直径6インチの金属Coターゲットの上に1cm角の SiO_2 ガラスチップを置いた複合ターゲットを用いた。このとき、ターゲットの片面の全表面積のうち10%を占めるように SiO_2 ガラスチップの量を調節した。真空槽を 5×10^{-6} Torrまで排気したのちにArガスを導入し、真空槽内部のガス圧が 2×10^{-2} TorrになるようにArガスの流量を調節し、600Wの高周波を入力してプラズマを発生させた。このときの成膜速度はおよそ 1 nm/sec であり、成膜時に基板を約200℃に加熱した。

【0024】成膜した複合薄膜の構造は図1と非常に良く似たものであり、Co結晶粒子が柱状に成長し、その粒界にアモルファスの SiO_2 が析出しており、この場合にはCo結晶の平均粒子径は約35nmとさらに大きいことがわかった。

【0025】この膜厚50nmの複合膜を0.003規定の硝酸水溶液に5分間浸漬してCo相を溶解除去した。実施例1の場合と同様に、Co相がほぼ完全に溶出し、粒界の SiO_2 がメッシュ状に残留していた。

【0026】実施例4

実施例1と同様の手順で、厚さ2mmのハステロイ基板上に金属Coと SiO_2 の2相からなる複合薄膜を形成した。スパッタには、直径6インチの金属Coターゲットの上に1cm角の SiO_2 ガラスチップを置いた複合ターゲットを用いた。このとき、ターゲットの片面の全表面積のうち10%を占めるように SiO_2 ガラスチップの量を調節した。真空槽を 5×10^{-6} Torrまで排気したのちにArガスを導入し、真空槽内部のガス圧が 2×10^{-2} TorrになるようにArガスの流量を調節し、600Wの高周波を入力してプラズマを発生させた。このときの成膜速度はおよそ 1 nm/sec であり、成膜時には基板の加熱やバイアス電圧の印加は行わなかった。

【0027】成膜した複合薄膜の構造は図1と非常に良く似たものであり、Co結晶粒子が柱状に成長し、その粒界にアモルファスの SiO_2 が析出しており、この場合のCo結晶の平均粒子径は約25nmであった。

【0028】この膜厚50nmの複合膜を0.003規定の硝酸水溶液に5分間浸漬してCo相を溶解除去した。実施例1の場合と同様に、Co相がほぼ完全に溶出し粒界の SiO_2 がメッシュ状に残留しており、ハステロイ基板からの膜の剥離は殆ど認められなかった。

【0029】実施例5

実施例1と同様の手順で、厚さ5mmのアルミナ基板上に金属Coと SiO_2 の2相からなる複合薄膜を形成した。スパッタには、直径6インチの金属Coターゲット

の上に1cm角の SiO_2 ガラスチップを置いた複合ターゲットを用いた。このとき、ターゲットの片面の全表面積のうち10%を占めるように SiO_2 ガラスチップの量を調節した。真空槽を 5×10^{-6} Torrまで排気したのちにArガスを導入し、真空槽内部のガス圧が 2×10^{-2} TorrになるようにArガスの流量を調節し、600Wの高周波を入力してプラズマを発生させた。このときの成膜速度はおよそ 1 nm/sec であり、成膜時には基板の加熱やバイアス電圧の印加は行わなかった。

【0030】成膜した複合薄膜の構造は図1と非常に良く似たものであり、Co結晶粒子が柱状に成長し、その粒界にアモルファスの SiO_2 が析出しており、Co結晶の平均粒子径は約19nmであった。

【0031】この膜厚50nmの複合膜を0.003規定の硝酸水溶液に5分間浸漬してCo相を溶解除去した。実施例1の場合と同様に、Co相がほぼ完全に溶出し、粒界の SiO_2 がメッシュ状に残留しており、アルミナ基板からの膜の剥離は殆ど認められなかった。

【0032】実施例6

実施例1と同様の手順で、厚さ0.8mmのポリエチレンフィルム基板上に金属Coと SiO_2 の2相からなる複合薄膜を形成した。スパッタには、直径6インチの金属Coターゲットの上に1cm角の SiO_2 ガラスチップを置いた複合ターゲットを用いた。このとき、ターゲットの片面の全表面積のうち10%を占めるように SiO_2 ガラスチップの量を調節した。真空槽を 5×10^{-6} Torrまで排気したのちにArガスを導入し、真空槽内部のガス圧が 2×10^{-2} TorrになるようにArガスの流量を調節し、600Wの高周波を入力してプラズマを発生させた。このときの成膜速度はおよそ0.8nm/secであり、成膜時には基板の加熱やバイアス電圧の印加は行わなかった。

【0033】成膜した複合薄膜の構造は図1と非常に良く似たものであり、Co結晶粒子が柱状に成長し、その粒界にアモルファスの SiO_2 が析出しており、Co結晶の平均粒子径は約26nmであった。

【0034】膜厚50nmの複合膜を0.003規定の硝酸水溶液に5分間浸漬してCo相を溶解除去した。実施例1の場合と同様に、Co相がほぼ完全に溶出し粒界の SiO_2 がメッシュ状に残留していた。ポリエチレンフィルムを基板とする場合、酸によるエッチング処理の過程でかなり顕著に膜の剥離が起こった。しかし、スパッタ法で複合膜を形成する前にポリエチレンフィルムの表面をコロナ放電処理あるいはシランカップリング剤で処理しておくことと剥離がかなり押さえられることがわかった。

【0035】実施例7

スパッタ法で100nmの厚さの金属Coを厚さ2mmの多孔質シリカ基板上に成膜した。成膜後の基板の表面

をダイヤモンド研磨装置で研磨し、シリカの細孔に詰まったC₆₀を残して基板上のC₆₀相を除去し、平滑な研磨面を得た。この基板の上に金属C₆₀とSiO₂の2相からなる複合薄膜を形成した。スパッタには、直径6インチの金属C₆₀ターゲットの上に1cm角のSiO₂ガラスチップを置いた複合ターゲットを用いた。このとき、ターゲットの片面の全表面積のうち10%を占めるようにSiO₂ガラスチップの量を調節した。真空槽を5×10⁻⁶Torrまで排気したのちにArガスを導入し、真空槽内部のガス圧が2×10⁻²TorrになるようにArガスの流量を調節し、600Wの高周波を入力してプラズマを発生させた。成膜速度はおよそ0.8nm/secであり、成膜時には基板の加熱やバイアス電圧の印加は行わなかった。

【0036】成膜した薄膜の構造は図1に非常に良く似たものであり、C₆₀結晶粒子が柱状に成長し、その粒界にアモルファスのSiO₂が析出しており、C₆₀結晶の平均粒子径は約26nmであった。

【0037】この膜厚50nmの複合膜を0.003規定の硝酸水溶液に5分間浸漬してシリカの細孔に詰まったC₆₀相とその上に形成したC₆₀-SiO₂複合膜中のC₆₀相を溶解除去した。実施例1の場合と同様に、C₆₀相がほぼ完全に溶出し、粒界のSiO₂がメッシュ状に残留しており、多孔質シリカ基板の細孔に詰まったC₆₀相もほぼ完全に除去されていることがわかった。また、多孔質シリカ基板からの複合膜の剝離は殆ど認められなかった。

【0038】実施例8

実施例1と同様の手順で、厚さ1.2mmのソーダライムガラス基板上に金属C₆₀とSiCの2相からなる複合薄膜を形成した。スパッタには、直径6インチの金属C₆₀ターゲットの上に1cm角のSiC結体チップを置いた複合ターゲットを用いた。このとき、ターゲットの片面の全表面積のうち20%を占めるようにSiC結体チップの量を調節した。真空槽を5×10⁻⁶Torrまで排気したのちにArガスを導入し、真空槽内部のガス圧が2×10⁻²TorrになるようにArガスの流量を調節し、600Wの高周波を入力してプラズマを発生させた。成膜速度はおよそ0.9nm/secであり、成膜時には基板の加熱やバイアス電圧の印加は行わなかった。

【0039】成膜した複合薄膜の構造は図1に非常に良く似たものであり、C₆₀結晶粒子が柱状に成長し、その粒界にアモルファスのSiCと考えられる相が析出した。このC₆₀結晶粒子の平均粒子径は約35nmであった。

【0040】膜厚50nmの複合膜を0.003規定の硝酸水溶液に5分間浸漬してC₆₀相を溶解除去した。実施例1の場合と同様に、C₆₀相がほぼ完全に溶出し、粒界のSiCがメッシュ状に残留していた。

【0041】実施例9

実施例1と同様の手順で、厚さ1.2mmのソーダライムガラス基板上に金属C₆₀とZrB₂の2相からなる複合薄膜を形成した。スパッタには、直径6インチの金属C₆₀ターゲットの上に1cm角のZrB₂セラミックスチップを置いた複合ターゲットを用いた。このとき、ターゲットの片面の全表面積のうち20%を占めるようにZrB₂セラミックスチップの量を調節した。真空槽を5×10⁻⁶Torrまで排気したのちにArガスを導入し、真空槽内部のガス圧が2×10⁻²TorrになるようにArガスの流量を調節し、600Wの高周波を入力してプラズマを発生させた。成膜速度はおよそ0.9nm/secであり、成膜時には基板の加熱やバイアス電圧の印加は行わなかった。

【0042】成膜した複合薄膜の構造は図1に非常に良く似たものであり、C₆₀結晶粒子が柱状に成長し、その粒界にアモルファスのZrB₂が析出しており、このC₆₀結晶粒子の平均粒子径は約21nmであった。

【0043】膜厚50nmの複合膜を0.003規定の硝酸水溶液に5分間浸漬してC₆₀相を溶解除去した。実施例1の場合と同様に、C₆₀相がほぼ完全に溶出し、粒界のZrB₂がメッシュ状に残留しており、ソーダライムガラス基板からの膜の剝離は殆ど認められなかった。

【0044】

【発明の効果】以上詳述したように、本発明は、膜の一方の表面からもう一方の表面に一次元的に貫通するナノメートルサイズの気孔を有する多孔質セラミックス膜であって、多孔質セラミックス膜がガラス、セラミックス、プラスチック又は耐熱金属の基板上に形成されていることを特徴とする多孔質セラミックス膜及びその製造方法に係るものであり、本発明によれば、圧力損失の少ない一次元貫通孔を有する多孔質セラミックス膜を提供することができる。また、本発明の多孔質セラミックス膜は多孔質セラミックス基板と組み合わせればセラミックスフィルタとして使用することができる。しかも、このセラミックスフィルタの材質は金属炭化物、金属炭化物、金属ホウ化物等から幅広く選べるので、2000℃付近の高耐熱性が要求される場合には金属炭化物、金属ホウ化物等の高融点材質を選択し、高温の酸化物雰囲気中で使用する場合には金属炭化物を選択するというように使い分けことができる。また、本発明の多孔質セラミックス膜をスパッタ法とエッチングで作製すれば、基板材料に金属、ガラス、セラミックスの他プラスチックなどの有機材料等殆ど全ての材料の基板上に多孔質セラミックス膜を形成することができる。また、複合膜をスパッタ法で成膜する場合には、基板の表面形状は平坦でなくとも成膜可能であり、数平方メートルに及び大面積の基板上に均一に成膜することも可能である。

【0045】本発明の多孔質セラミックス膜と多孔質セラミックス膜を多孔質セラミックス基板と組み合わせた

セラミックスフィルタは単なるガス分離膜としてだけでなく、細孔径を目的に合わせて制御すれば一般の工場排気、火力発電所の排気ガス、自動車の排気ガス中に含まれる有害な微粒子の除去等に使用できる。また、液体中の微細粒子状物質、例えば、ウイルスのような極微小な微生物の分離、溶液中に分散したコロイド状分子集団の分離、特定の分子のふるい分け等にも使用することができる。

【0046】さらに、膜の貫通気孔の表面を無機あるいは有機の触媒で修飾すれば、より活性の高い触媒膜を得ることが可能である。

【図面の簡単な説明】

【図1】 Co-SiO_2 系試作試料を透過型電子顕微鏡により膜面に垂直な方向から観察した拡大写真。

【図2】本発明の多孔質セラミックス膜を多孔質セラミックス基板上に形成する手順の概略図。

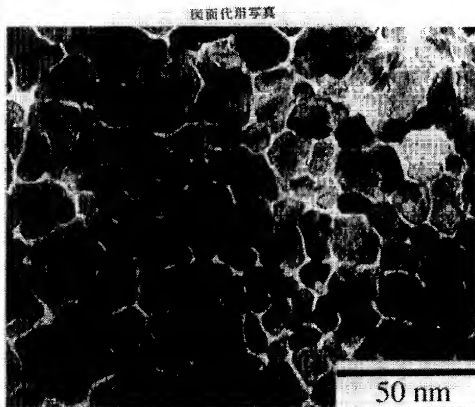
【図3】本発明において、ソーダライムガラス基板上に Co-SiO_2 複合膜をスパッタ法で作成した後 0.03 規定の硝酸でエッチングしたものを膜の断面方向から見た走査型電子顕微鏡写真。

【図4】本発明による多孔質セラミックス膜の概要を示す斜視図。

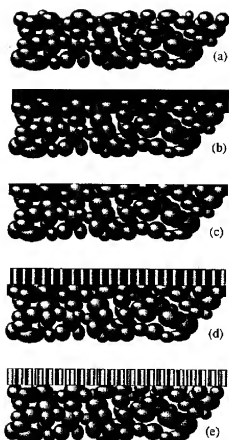
【符号の説明】

- (a) 多孔質セラミックス基板の断面図
- (b) セラミックス基板上に金属膜を形成した状況
(基板表面の細孔は金属で充填される)
- (c) セラミックス基板表面が現れるまで表面を研磨した状態
- (d) (c) で得られた膜の上に本発明の金属・セラミックス複合膜を形成した状態
- (e) 酸によるエッチングで金属を溶出した後の状態

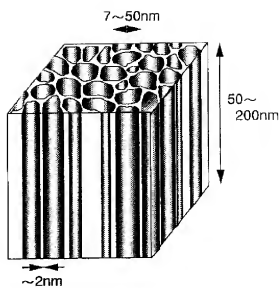
【図1】



【図2】



【図4】



【図3】



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(54) **POROUS CERAMIC FILM AND ITS PRODUCTION**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide ceramic filters having various compositions, each of which is provided with one-dimensional through-pores low in pressure drop and is appropriately used for separating molecules or fine particles.

SOLUTION: This ceramic film is provided with one-dimensional through-pores each of which extends from one surface of the film to the other and has a pore size of a few nanometers, and produced on a substrate made of glass, a ceramic material, plastic material or heat-resistant metal by forming a composite film consisting of a ceramic phase and a metallic phase with a vapor growth method and then, removing the metallic phase in the composite film with an etching method. Thus, the objective porous ceramic film provided with one-dimensional through-pores each having a pore size of the order of a few nanometers can be synthesized with good reproducibility. Also, by forming such ceramic films on various substrates, ceramic filters each of which shows an excellent function capable of separating molecules or fine particles each having a size of a few nanometers can be manufactured.

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CLAIMS

[Claim(s)]

[Claim 1] Porous-ceramics film which is porous-ceramics film which has the pore of the nano meter size which penetrates the metal phase in the bipolar membrane which consists of a ceramic phase which formed membranes by vapor growth, and a metal phase in single dimension on another front face from one [which is removed and obtained] membranous front face, and is characterized by forming the porous-ceramics film concerned on the substrate of glass, the ceramics, plastics, or a heat-resistant metal.

[Claim 2] Porous-ceramics film according to claim 1 which is a compound more than a kind as which said porous-ceramics film is chosen from a metallic oxide, metallic carbide, and a metal boride.

[Claim 3] Porous-ceramics film according to claim 1 or 2 whose substrate which supports said porous-ceramics film is a porous body.

[Claim 4] Porous-ceramics film according to claim 1 whose average aperture of said pore penetrated in single dimension is 5-100 nanometers.

[Claim 5] The manufacture approach of the porous-ceramics film of having the pore of the nano meter size penetrated in single dimension on another front face from one front face of the film characterized by forming on a substrate the bipolar membrane which consists of a ceramic phase and a metal phase, and subsequently removing the metal phase in bipolar membrane by etching by vapor growth.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the porous-ceramics film and its manufacture approach. In more detail, this invention relates to the approach of manufacturing the porous-ceramics film and the porous-ceramics film concerned of various presentations which have the single dimension penetration pore with little pressure loss used suitably with sufficient repeatability, in order to separate a molecule and a particle. The porous-ceramics film of this invention is useful as a separation means of the molecule of various kinds [discover / the isolation in nano meter size], or a particle etc.

[0002]

[Description of the Prior Art] The ceramic filter excellent in thermal resistance and corrosion resistance aiming at separating the molecule contained in hot gas or a corrosive liquid and a particle is developed. As an approach of producing a porous-ceramics object or the porous-ceramics film, ceramic raw material fine particles are sintered and many methods of using the open pore (free passage pore which carries out opening to the front face of a ceramic object) formed in the process in which a ceramic object carries out eburnation as it is are adopted (JP,7-8729,A). However, by the ceramic object which carried out in this way and was produced, or the ceramic film, there was a problem that it was difficult to arrange the size of a pore diameter, and it difficult to produce the pore of

nanometer order with sufficient repeatability.

[0003] Although the porosity silica is produced by the technique of having considered as the attempt which produces the porous body which has the pole diameter to which nanometer order was equal with sufficient repeatability, and having combined a sol-gel method and spinodal decomposition (Nakanishi et al., "Ceramic Transactions and Porous Materials", The American Ceramics Society, and 51-60 (1992)), the organization where the silica phase was connected in the shape of a mesh in this case is formed, the configuration of pore is irregular, and that direction is random.

[0004] Thus, since many ceramic parts into which the configurations of pore are scattered on in the molecule and particle which move in the filtration direction that it is irregular and the direction is non-orientation, and bar migration existed, there was a problem which pressure loss generates.

[0005] In order to solve the above-mentioned problem, development of the ceramic film which has the pore (it may be hereafter called single dimension penetration pore) which a pole diameter is nano meter size and moreover penetrates in single dimension is tried. As the typical example, there is porosity alumina film by anodic oxidation of aluminum (JP,6-37291,B). A pole diameter can control the film produced by anodic oxidation of aluminum by the production condition in several nm to dozens of nm, and since a membranous presentation is an alumina, it has the advantage that considerable thermal resistance and corrosion resistance are expectable. However, in the case of the porosity alumina film by anodic oxidation, there is a fault that it is restricted to the alumina of amorphism with the film stable only near ordinary temperature obtained, and only an aluminum plate can be chosen from the constraint on the principle of using anodic oxidation in the electrolytic solution of an aluminum plate with metal aluminium foil or thickness, as a substrate.

[0006] As the approach of compensating the fault of the porosity alumina film by the above-mentioned anodic oxidation, the approach of imprinting a pore pattern to a polymer membrane is tried, using as mold the porosity alumina film produced by anodic oxidation (Masuda et al.; Ceramic Society of Japan, 1995 spring annual convention drafts, p485 3F4 01). However, there is a fault that it is difficult to stick the membrane which the ingredient which imprints the structure of the porosity alumina film by anodic oxidation in this case is restricted to the organic substance, and imprinted membrane structure on other substrates, and to consider as new bipolar membrane.

[0007]

[Problem(s) to be Solved by the Invention] The purpose of this invention cancels the above-mentioned fault which the conventional technique has, and is to offer the porous-ceramics film which has the single dimension penetration pore of available nano meter size in a gas separation membrane or a catalyst with various ceramic ingredients (a metallic oxide, metallic carbide, or metal boride). Furthermore, it is in offering the new bipolar membrane in which various kinds of porous-ceramics film was formed on the substrate of the substantia compacta or porosity which consists of glass, the ceramics, plastics, or a heat-resistant metal, and offering the approach of manufacturing such ceramic film with sufficient repeatability.

[0008]

[Means for Solving the Problem] It is the porous-ceramics film which has the pore of the nano meter size penetrated in single dimension on another front face from one

membranous front face which this invention is made that the aforementioned technical problem should be solved, and the porous-ceramics film of this invention removes the metal phase in the bipolar membrane which consists of a ceramic phase which formed membranes by vapor growth, and a metal phase, and is obtained, and is characterized by to form the porous-ceramics film concerned on the substrate of glass, the ceramics, plastics, or a heat-resistant metal. The desirable porous-ceramics film by this invention is at least one kind of compound with which the matter which constitutes the aforementioned porous-ceramics film was chosen from a metallic oxide, metallic carbide, and a metal boride. The substrate with which other desirable porous-ceramics film of this invention supports said porous-ceramics film is a porous body. The average aperture of said pore penetrated in single dimension of other desirable porous-ceramics film of this invention is 5-100 nanometers. The manufacture approach of the porous-ceramics film of this invention is characterized by forming on a substrate the bipolar membrane which consists of a ceramic phase and a metal phase, and subsequently removing the metal phase in bipolar membrane by etching by vapor growth.

[0009]

[Embodiment of the Invention] Then, this invention is further explained to a detail. That is, the porous-ceramics film of this invention is produced in two steps of processes. On a first stage story, the film on which the metal and the ceramic ingredient (a metallic oxide, metallic carbide, or metal boride) were intermingled on the nano meter scale using vapor growth, such as a spatter, is produced. At this time, the detailed organization for which the ceramic ingredient enclosed the surroundings of the metal phase which grew in the shape of a column is formed by controlling the mixing ratio and membrane formation conditions of the metal phase and ceramic ingredient to be used (drawing 1). In this invention, it is possible to change an aperture with the particle size of a metal phase. In this case, the mean particle diameter of a metal phase is changeable in about 5-500nm with the volume fraction and membrane formation conditions of a metal phase and a ceramic phase (substrate temperature, residual-gas pressure at the time of a spatter, etc.). Moreover, the thickness of the grain boundary phase which remains as a ceramic filter part can be changed with the volume fraction of a metal phase and a ceramic phase. Therefore, it is possible to change a film presentation and membrane formation conditions independently as a parameter in the case of producing the film, and the thickness of an average of a grain boundary phase can be changed by about about 1-50nm. SiO₂ to which the part which looks dark in drawing 1 is Co crystal grain, and the part of the shape of a white mesh deposited in the grain boundary of Co crystal grain It is a part. The mean particle diameter of Co crystal grain is about 12nm and SiO₂. The width of face of a grain boundary layer is about 2nm. Membrane structure similar to this is a Co-Pt system alloy and SiO₂ with the magnetic film of a hard magnetic disk. It has realized by mixed stock (Japanese Patent Application No. No. 51410 [seven to]). Then, the porous-ceramics film which finally has the penetration pore of a single dimension is obtained by removing a metal part using an acid or alkali on a second stage story. The schematic diagram of the procedure which forms the porous-ceramics film of this invention on a porous-ceramics substrate is shown in drawing 2 . The situation that (a) formed the sectional view of a porous-ceramics substrate on the ceramic substrate among drawing, and (b) formed the metal membrane (the pore on the front face of a substrate is filled up with a metal), As for (c), the condition which ground the front face, the

condition in which the metal and ceramic bipolar membrane of this invention were formed on the film with which (d) was obtained by (c), and the condition after (e) is eluted in a metal by etching by the acid are shown, respectively until a ceramic substrate front face appears.

[0010] As vapor growth used on a first stage story, although a sputter, vacuum deposition, a CVD method, the laser ablation method, or a molecular beam epitaxy method can be considered, it is desirable to use a sputter in consideration of mass-production nature or the possibility of large area membrane formation.

[0011] As a combination of a metal and a ceramic ingredient, a metal and a ceramic ingredient should just be the combination which starts phase separation at the time of membrane formation. The metal or the alloy which is the metal which is easy to grow in the shape of a column as a metal phase, and dissolves easily in an acid and alkali and which binding energy with oxygen, carbon, and boron is easy to return to it small in order to use the ceramic phase which deposited into the grain boundary part of the metal phase which grew in the shape of a column for the pore part after etching the metal phase which grows in the shape of a column in this invention as a residual phase is desirable. More than a kind chosen from the alloy which makes a principal component alkaline earth metal, such as an alloy and Mg, and it which make a principal component 3d transition metals, such as V, Cr, Mn, nickel, Fe, Co, Cu, and Zn, and them in consideration of the ease of the handling at the time of a sputter practical is suitable. In addition, aluminum, In, Sn, Pb, etc. are available. As a ceramic phase used as a residual phase, more than a kind chosen from borides, such as carbide, such as oxide, such as an alumina, a mullite, cordierite, a spinel, a zeolite, and forsterite, silicon carbide, titanium carbide, and zirconium carbide, titanium boride, zirconium boride, and boron carbide, can use suitably.

[0012] When forming the bipolar membrane of the above-mentioned metal and the ceramics by a sputter etc., on a metal target, the wafer of ceramic ingredients, such as a metallic oxide, metallic carbide, and a metal boride, can be placed, and it can use as a multicomponent target. Still more preferably, in order to make small dispersion in a presentation inside the film after membrane formation, the composite material mixed to homogeneity by the powder metallurgy-approach at the time of target production is prepared.

[0013] The substrate used in case the above porous-ceramics film is manufactured can be chosen from glass, the ceramics, plastics, and a heat-resistant metal, and can also use not a still more precise substrate but a porous substrate. As a heat-resistant metal used for a substrate, oxidation-resistant alloys, such as stainless steel which consists of Fe, nickel, Cr, V, etc., and Hastelloy, are suitable. Drawing 2 shows how to form membranes, using a porous-ceramics substrate as an example. That is, the front face is ground in the condition of having sunk a metal or resin into the front face of the ceramic porous body of dozens of micron meter from the several nm average aperture, and a smooth front face is formed. Subsequently, this front face is washed using water, a surfactant, an organic solvent, etc., and the sputter film is formed on it by making this into a substrate. At this time, it is desirable to use what is removed on the etching conditions same as the metal which sinks in, or resin as the ingredient of the above-mentioned metal target.

[0014] Next, with an acid or an alkali solution, etching processing is carried out and the metal component in the obtained bipolar membrane is removed. It is desirable to choose

suitably according to the class of metal which can use a sulfuric acid, a hydrochloric acid, a nitric acid, oxalic acid, an acetic acid, etc., and should be carried out elution as an acid used by this etching processing. Since the ceramic part formed of the first membrane formation process has many amorphous or things which have low extent of crystallization, it is desirable to etch on weak etching conditions using the fully diluted solution. For example, Co is used as a metal component and it is SiO₂ as a ceramic component. When using, it is desirable to process with the etch rate of 0.3nm/s using the nitric-acid water solution of 0.003 conventions.

[0015] As stated above, in case the manufacture approach of the porous-ceramics film of this invention forms the porous-ceramics film, it produces the bipolar membrane of a metal and the ceramics by vapor growth, it is characterized by using combining the approach etching subsequently removes a metal phase, and can offer the various porous-ceramics film which has new structure and a new presentation. As for the porous-ceramics film of this invention, it is possible to make the isolation in nano meter size discover, and it is useful as a filter for separating a molecule and a particle etc. The porous-ceramics film of this invention can control independently the width of face of a pole diameter and a grain boundary phase (thicken width of face of a grain boundary phase especially), and essentially differs from the conventional anodic oxidation alumina film etc. at this point.

[0016]

[Function] When the two phase from which the chemical durability which consists of a metal and ceramics (a metallic oxide, a metal boride, metallic carbide) differs by the forming-membranes methods, such as a sputter, in this invention forms the bipolar membrane intermingled with nanometer order, subsequently removes only a metal part by acid etching etc. and makes a ceramic part remain, it becomes possible to compound the porous-ceramics film which has single dimension penetration pore with little pressure loss. That is, by controlling membrane formation conditions appropriately, the metal phase which is one of the main membrane components is grown up in the shape of a column, a ceramic ingredient is deposited in the grain boundary, and it becomes possible by removing a metal phase by etching further to obtain the porous-ceramics film which has the single dimension penetration pore of the pole diameter of nanometer order.

[0017] Moreover, in order to form the bipolar membrane before carrying out acid etching by a sputter etc., it becomes available [the thing of a variety and various ingredients, such as a metal, glass, ceramics, and plastics, and a gestalt] at the substrate which supports the film.

[0018]

[Example] An example explains this invention concretely below.

They are metals Co and SiO₂ on a soda lime glass substrate with an example 1 thickness of 1.2mm. The compound thin film which consists of two phases was formed. In a sputter, it is SiO₂ of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO₂ so that 20% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10⁻⁶Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might serve as 2x10⁻²Torr, the RF of 600W was inputted, and the plasma was generated. The membrane formation rate at this time is about 1 nm/sec, and neither

substrate heating nor impression of bias voltage was performed at the time of membrane formation.

[0019] The structure of the compound thin film which formed membranes is shown in the transmission electron microscope photograph of drawing 1. Drawing 1 is the enlargement which carried out grinding of the glass substrate, removed it, carried out ion polish of the bipolar membrane further, made thin, and was seen from the direction perpendicular to a film surface. With this photograph, Co crystal grain child with a mean particle diameter of 12nm is growing in the shape of a column, and it is SiO₂ amorphously to a grain boundary. It deposits.

[0020] Next, it was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of thickness produced by the above-mentioned approach for 5 minutes, and dissolution removal of the Co phase was carried out. Drawing 3 is the enlargement which observed the film after carrying out dissolution removal of this Co phase with the scanning electron microscope. Co phase is eluted nearly completely and it is SiO₂ of a grain boundary. It remained in the shape of a mesh. Expansion of the ceramic film obtained by drawing 4 by doing in this way and an example of a perspective view are shown.

[0021] By the same procedure as example 2 example 1, they are metals Co and SiO₂ on a soda lime glass substrate with a thickness of 1.2mm. The compound thin film which consists of two phases was formed. In a spatter, it is SiO₂ of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO₂ so that 10% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10⁻⁶Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10⁻²Torr, the RF of 600W was inputted, and the plasma was generated. The membrane formation rate at this time is about 1 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0022] Drawing 1 is resembled very well, the crystal grain child of Co grows in the shape of a column, and the structure of the compound thin film which formed membranes is SiO₂ amorphous to that grain boundary. It deposited and the mean particle diameter of Co crystal was large a little with about 20nm in this case. It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of this thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is SiO₂ of a grain boundary. It remained in the shape of a mesh.

[0023] By the same procedure as example 3 example 1, they are metals Co and SiO₂ on a soda lime glass substrate with a thickness of 1.2mm. The compound thin film which consists of two phases was formed. In a spatter, it is SiO₂ of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO₂ so that 10% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10⁻⁶Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10⁻²Torr, the RF of 600W was inputted, and the plasma was generated. The membrane formation rate at this time is about 1 nm/sec, and heated the substrate at about 200 degrees C at the time of membrane

formation.

[0024] Drawing 1 is resembled very well, Co crystal grain child grows in the shape of a column, and the structure of the compound thin film which formed membranes is SiO₂ amorphous to that grain boundary. It deposited and it turned out [about 35nm and] that the mean particle diameter of Co crystal is still larger in this case.

[0025] It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of this thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is SiO₂ of a grain boundary. It remained in the shape of a mesh.

[0026] By the same procedure as example 4 example 1, they are metals Co and SiO₂ on the Hastelloy substrate with a thickness of 2mm. The compound thin film which consists of two phases was formed. In a sputter, it is SiO₂ of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO₂ so that 10% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10⁻⁶Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10⁻²Torr, the RF of 600W was inputted, and the plasma was generated. The membrane formation rate at this time is about 1 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0027] It is very well alike in drawing 1, Co crystal grain child grows in the shape of a column, and the structure of the compound thin film which formed membranes is SiO₂ amorphous to that grain boundary. It deposited and the mean particle diameter of Co crystal in this case was about 25nm.

[0028] It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of this thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is SiO₂ of a grain boundary. It remained in the shape of a mesh, and most exfoliations of the film from the Hastelloy substrate were not accepted.

[0029] In the same procedure as example 5 example 1, the compound thin film which consists of two phases of metals Co and SiO₂ was formed on the alumina substrate with a thickness of 5mm. In a sputter, it is SiO₂ of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO₂ so that 10% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10⁻⁶Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10⁻²Torr, the RF of 600W was inputted, and the plasma was generated. The membrane formation rate at this time is about 1 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0030] It is very well alike in drawing 1, Co crystal grain child grows in the shape of a column, and the structure of the compound thin film which formed membranes is SiO₂ amorphous to the grain boundary. It deposited and the mean particle diameter of Co crystal was about 19nm.

[0031] It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of this thickness for 5 minutes, and dissolution removal of the

Co phase was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is SiO₂ of a grain boundary. It remained in the shape of a mesh, and most exfoliations of the film from an alumina substrate were not accepted.

[0032] By the same procedure as example 6 example 1, they are metals Co and SiO₂ on a polyethylene film substrate with a thickness of 0.8mm. The compound thin film which consists of two phases was formed. In a sputter, it is SiO₂ of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO₂ so that 10% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10⁻⁶Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10⁻²Torr, the RF of 600W was inputted, and the plasma was generated. The membrane formation rates at this time are about 0.8 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0033] It is very well alike in [drawing 1](#), Co crystal grain child grows in the shape of a column, and the structure of the compound thin film which formed membranes is SiO₂ amorphous to the grain boundary. It deposited and the mean particle diameter of Co crystal was about 26nm.

[0034] It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is SiO₂ of a grain boundary. It remained in the shape of a mesh. When a polyethylene film was used as a substrate, exfoliation of the film took place quite notably in process of the etching processing by the acid. However, when the front face of a polyethylene film was processed by corona discharge treatment or the silane coupling agent before forming bipolar membrane by the sputter, it turned out that exfoliation is pressed down considerably.

[0035] The metal Co with a thickness of 100nm was formed on the porosity silica substrate with a thickness of 2mm by example 7 sputter. The front face of the substrate after membrane formation was ground with diamond polish equipment, it left Co got blocked in the pore of a silica, Co phase on a substrate was removed, and the smooth polished surface was acquired. They are metals Co and SiO₂ on this substrate. The compound thin film which consists of two phases was formed. In a sputter, it is SiO₂ of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO₂ so that 10% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10⁻⁶Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10⁻²Torr, the RF of 600W was inputted, and the plasma was generated. Membrane formation rates are about 0.8 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0036] It is very well alike in [drawing 1](#), Co crystal grain child grows in the shape of a column, and the structure of the thin film which formed membranes is SiO₂ amorphous to the grain boundary. It deposited and the mean particle diameter of Co crystal was about 26nm.

[0037] Co phase which was immersed in the nitric-acid water solution of 0.003

conventions of the bipolar membrane of 50nm of this thickness for 5 minutes, and was got blocked in the pore of a silica, and Co-SiO₂ formed on it Dissolution removal of the Co phase in bipolar membrane was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is SiO₂ of a grain boundary. It is ***** to be removed nearly completely [Co phase which remained in the shape of a mesh and was got blocked in the pore of a porosity silica substrate]. Moreover, most exfoliations of the bipolar membrane from a porosity silica substrate were not accepted.

[0038] In the same procedure as example 8 example 1, the compound thin film which consists of two phases of Metals Co and SiC was formed on the soda lime glass substrate with a thickness of 1.2mm. The multicomponent target which placed the SiC sintered compact tip of 1cm angle on the metal Co target with a diameter of 6 inches was used for the spatter. At this time, the amount of a SiC sintered compact chip was adjusted so that 20% of the total surface area of one side of a target might be occupied. After exhausting a vacuum tub to 5x10⁻⁶Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10⁻²Torr, the RF of 600W was inputted, and the plasma was generated. Membrane formation rates are about 0.9 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0039] The structure of the compound thin film which formed membranes was very well alike in drawing 1 , Co crystal grain child grew in the shape of a column, and the phase considered to be amorphous SiC by the grain boundary deposited. This Co crystal grain child's mean particle diameter was about 35nm.

[0040] It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase was eluted nearly completely and SiC of a grain boundary remained in the shape of a mesh.

[0041] By the same procedure as example 9 example 1, they are metals Co and ZrB₂ on a soda lime glass substrate with a thickness of 1.2mm. The compound thin film which consists of two phases was formed. In a spatter, it is ZrB₂ of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the ceramic tip was used. At this time, it is ZrB₂ so that 20% of the total surface area of one side of a target may be occupied. The amount of a ceramic chip was adjusted. After exhausting a vacuum tub to 5x10⁻⁶Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10⁻²Torr, the RF of 600W was inputted, and the plasma was generated. Membrane formation rates are about 0.9 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0042] It is very well alike in drawing 1 , Co crystal grain child grows in the shape of a column, and the structure of the compound thin film which formed membranes is ZrB₂ amorphous to that grain boundary. It deposited and this Co crystal grain child's mean particle diameter was about 21nm.

[0043] It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is ZrB₂ of a grain boundary. It remained in the shape of a mesh, and most exfoliations of the film from a soda lime glass substrate were not accepted.

[0044]

[Effect of the Invention] As explained in full detail above, it is the porous-ceramics film which has the pore of the nano meter size penetrated in single dimension on another front face from one membranous front face, this invention relates to the porous-ceramics film characterized by forming the porous-ceramics film on the substrate of glass, the ceramics, plastics, or a heat-resistant metal, and its manufacture approach, and according to this invention, it can offer the porous-ceramics film which has a single dimension through tube with little pressure loss. Moreover, the porous-ceramics film of this invention can be used as a ceramic filter, if it combines with a porous-ceramics substrate. And since the quality of the material of this ceramic filter can be broadly chosen from a metallic oxide, metallic carbide, a metal boride, etc., it can use properly as it chooses the high-melting quality of the materials, such as metallic carbide and a metal boride, when the high thermal resistance near 2000 degree C is required, and it chooses a metallic oxide, in using it in a hot oxidizing atmosphere. Moreover, if the porous-ceramics film of this invention is produced by the spatter and etching, the porous-ceramics film can be formed at a substrate ingredient on the substrate of almost all ingredients, such as organic materials, such as other plastics of a metal, glass, and the ceramics. Moreover, when forming bipolar membrane by the spatter, it is also possible to form membranes to homogeneity on the substrate of the large area which can form membranes even if the shape of surface type of a substrate is not flat, and amounts to several square meters.

[0045] The ceramic filter which combined the porous-ceramics film and porous-ceramics film of this invention with the porous-ceramics substrate is applicable to removal of the harmful particle contained in general works exhaust air, the exhaust gas of a thermal power station, and the exhaust gas of an automobile etc., if it controls [for the purpose of a pole diameter] only as a mere gas separation membrane. Moreover, it can be used for separation of the very fine particle-like matter in a liquid, for example, a very minute microorganism like a virus, the separation of a colloid molecule ensemble distributed in the solvent, sieving of a specific molecule, etc.

[0046] Furthermore, if the front face of membranous penetration pore is embellished with an inorganic or organic catalyst, it is possible to obtain the catalyst film with more high activity.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the porous-ceramics film and its manufacture approach. In more detail, this invention relates to the approach of manufacturing the porous-ceramics film and the porous-ceramics film concerned of various presentations which have the single dimension penetration pore with little pressure loss used suitably with sufficient repeatability, in order to separate a molecule and a particle. The porous-ceramics film of this invention is useful as a separation means of the molecule of various kinds [discover / the isolation in nano meter size], or a particle etc.

PRIOR ART

[Description of the Prior Art] The ceramic filter excellent in thermal resistance and corrosion resistance aiming at separating the molecule contained in hot gas or a corrosive liquid and a particle is developed. As an approach of producing a porous-ceramics object or the porous-ceramics film, ceramic raw material fine particles are sintered and many methods of using the open pore (free passage pore which carries out opening to the front face of a ceramic object) formed in the process in which a ceramic object carries out eburation as it is are adopted (JP,7-8729,A). However, by the ceramic object which carried out in this way and was produced, or the ceramic film, there was a problem that it was difficult to arrange the size of a pore diameter, and it difficult to produce the pore of nanometer order with sufficient repeatability.

[0003] Although the porosity silica is produced by the technique of having considered as the attempt which produces the porous body which has the pore diameter to which nanometer order was equal with sufficient repeatability, and having combined a sol-gel method and spinodal decomposition (Nakanishi et al., "Ceramic Transactions and Porous Materials", The American Ceramics Society, and 51-60 (1992)), the organization where the silica phase was connected in the shape of a mesh in this case is formed, the configuration of pore is irregular, and that direction is random.

[0004] Thus, since many ceramic parts into which the configurations of pore are scattered on in the molecule and particle which move in the filtration direction that it is irregular and the direction is non-orientation, and bar migration existed, there was a problem which pressure loss generates.

[0005] In order to solve the above-mentioned problem, development of the ceramic film which has the pore (it may be hereafter called single dimension penetration pore) which a pore diameter is nano meter size and moreover penetrates in single dimension is tried. As the typical example, there is porosity alumina film by anodic oxidation of aluminum (JP,6-37291,B). A pore diameter can control the film produced by anodic oxidation of aluminum by the production condition in several nm to dozens of nm, and since a membranous presentation is an alumina, it has the advantage that considerable thermal resistance and corrosion resistance are expectable. However, in the case of the porosity alumina film by anodic oxidation, there is a fault that it is restricted to the alumina of amorphism with the film stable only near ordinary temperature obtained, and only an aluminum plate can be chosen from the constraint on the principle of using anodic oxidation in the electrolytic solution of an aluminum plate with metal aluminium foil or thickness, as a substrate.

[0006] As the approach of compensating the fault of the porosity alumina film by the above-mentioned anodic oxidation, the approach of imprinting a pore pattern to a polymer membrane is tried, using as mold the porosity alumina film produced by anodic oxidation (Masuda et al.; Ceramic Society of Japan, 1995 spring annual convention drafts, p485 3F4 01). However, there is a fault that it is difficult to stick the membrane which the ingredient which imprints the structure of the porosity alumina film by anodic oxidation in this case is restricted to the organic substance, and imprinted membrane structure on other substrates, and to consider as new bipolar membrane

[Effect of the Invention] As explained in full detail above, it is the porous-ceramics film which has the pore of the nano meter size penetrated in single dimension on another front face from one membranous front face, this invention relates to the porous-ceramics film characterized by forming the porous-ceramics film on the substrate of glass, the ceramics, plastics, or a heat-resistant metal, and its manufacture approach, and according to this invention, it can offer the porous-ceramics film which has a single dimension through tube with little pressure loss. Moreover, the porous-ceramics film of this invention can be used as a ceramic filter, if it combines with a porous-ceramics substrate. And since the quality of the material of this ceramic filter can be broadly chosen from a metallic oxide, metallic carbide, a metal boride, etc., it can use properly as it chooses the high-melting quality of the materials, such as metallic carbide and a metal boride, when the high thermal resistance near 2000 degree C is required, and it chooses a metallic oxide, in using it in a hot oxidizing atmosphere. Moreover, if the porous-ceramics film of this invention is produced by the spatter and etching, the porous-ceramics film can be formed at a substrate ingredient on the substrate of almost all ingredients, such as organic materials, such as other plastics of a metal, glass, and the ceramics. Moreover, when forming bipolar membrane by the spatter, it is also possible to form membranes to homogeneity on the substrate of the large area which can form membranes even if the shape of surface type of a substrate is not flat, and amounts to several square meters. [0045] The ceramic filter which combined the porous-ceramics film and porous-ceramics film of this invention with the porous-ceramics substrate is applicable to removal of the harmful particle contained in general works exhaust air, the exhaust gas of a thermal power station, and the exhaust gas of an automobile etc., if it controls [for the purpose of a pole diameter] only as a mere gas separation membrane. Moreover, it can be used for separation of the very fine particle-like matter in a liquid, for example, a very minute microorganism like a virus, the separation of a colloid molecule ensemble distributed in the solvent, sieving of a specific molecule, etc. [0046] Furthermore, if the front face of membranous penetration pore is embellished with an inorganic or organic catalyst, it is possible to obtain the catalyst film with more high activity

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The purpose of this invention cancels the above-mentioned fault which the conventional technique has, and is to offer the porous-ceramics film which has the single dimension penetration pore of available nano meter size in a gas separation membrane or a catalyst with various ceramic ingredients (a metallic oxide, metallic carbide, or metal boride). Furthermore, it is in offering the new bipolar membrane in which various kinds of porous-ceramics film was formed on the substrate of the substantia compacta or porosity which consists of glass, the ceramics, plastics, or a heat-resistant metal, and offering the approach of manufacturing such ceramic film with sufficient repeatability.

MEANS

[Means for Solving the Problem] It is the porous-ceramics film which has the pore of the nano meter size penetrated in single dimension on another front face from one membranous front face which this invention is made that the aforementioned technical problem should be solved, and the porous-ceramics film of this invention removes the metal phase in the bipolar membrane which consists of a ceramic phase which formed membranes by vapor growth, and a metal phase, and is obtained, and is characterized by to form the porous-ceramics film concerned on the substrate of glass, the ceramics, plastics, or a heat-resistant metal. The desirable porous-ceramics film by this invention is at least one kind of compound with which the matter which constitutes the aforementioned porous-ceramics film was chosen from a metallic oxide, metallic carbide, and a metal boride. The substrate with which other desirable porous-ceramics film of this invention supports said porous-ceramics film is a porous body. The average aperture of said pore penetrated in single dimension of other desirable porous-ceramics film of this invention is 5-100 nanometers. The manufacture approach of the porous-ceramics film of this invention is characterized by forming on a substrate the bipolar membrane which consists of a ceramic phase and a metal phase, and subsequently removing the metal phase in bipolar membrane by etching by vapor growth.

[0009]

[Embodiment of the Invention] Then, this invention is further explained to a detail. That is, the porous-ceramics film of this invention is produced in two steps of processes. On a first stage story, the film on which the metal and the ceramic ingredient (a metallic oxide, metallic carbide, or metal boride) were intermingled on the nano meter scale using vapor growth, such as a spatter, is produced. At this time, the detailed organization for which the ceramic ingredient enclosed the surroundings of the metal phase which grew in the shape of a column is formed by controlling the mixing ratio and membrane formation conditions of the metal phase and ceramic ingredient to be used (drawing 1). In this invention, it is possible to change an aperture with the particle size of a metal phase. In this case, the mean particle diameter of a metal phase is changeable in about 5-500nm with the volume fraction and membrane formation conditions of a metal phase and a ceramic phase (substrate temperature, residual-gas pressure at the time of a spatter, etc.). Moreover, the thickness of the grain boundary phase which remains as a ceramic filter part can be changed with the volume fraction of a metal phase and a ceramic phase. Therefore, it is possible to change a film presentation and membrane formation conditions independently as a parameter in the case of producing the film, and the thickness of an average of a grain boundary phase can be changed by about about 1-50nm. SiO₂ to which the part which looks dark in drawing 1 is Co crystal grain, and the part of the shape of a white mesh deposited in the grain boundary of Co crystal grain It is a part. The mean particle diameter of Co crystal grain is about 12nm and SiO₂. The width of face of a grain boundary layer is about 2nm. Membrane structure similar to this is a Co-Pt system alloy and SiO₂ with the magnetic film of a hard magnetic disk. It has realized by mixed stock (Japanese Patent Application No. No. 51410 [seven to J]). Then, the porous-ceramics film which finally has the penetration pore of a single dimension is obtained by removing a metal part using an acid or alkali on a second stage story. The schematic diagram of the procedure which forms the porous-ceramics film of this invention on a porous-ceramics substrate is shown in drawing 2 . The situation that (a) formed the sectional view of a porous-ceramics substrate on the ceramic substrate among

drawing, and (b) formed the metal membrane (the pore on the front face of a substrate is filled up with a metal), As for (c), the condition which ground the front face, the condition in which the metal and ceramic bipolar membrane of this invention were formed on the film with which (d) was obtained by (c), and the condition after (e) is eluted in a metal by etching by the acid are shown, respectively until a ceramic substrate front face appears.

[0010] As vapor growth used on a first stage story, although a spatter, vacuum deposition, a CVD method, the laser ablation method, or a molecular beam epitaxy method can be considered, it is desirable to use a spatter in consideration of mass-production nature or the possibility of large area membrane formation.

[0011] As a combination of a metal and a ceramic ingredient, a metal and a ceramic ingredient should just be the combination which starts phase separation at the time of membrane formation. The metal or the alloy which is the metal which is easy to grow in the shape of a column as a metal phase, and dissolves easily in an acid and alkali and which binding energy with oxygen, carbon, and boron is easy to return to it small in order to use the ceramic phase which deposited into the grain boundary part of the metal phase which grew in the shape of a column for the pore part after etching the metal phase which grows in the shape of a column in this invention as a residual phase is desirable. More than a kind chosen from the alloy which makes a principal component alkaline earth metal, such as an alloy and Mg, and it which make a principal component 3d transition metals, such as V, Cr, Mn, nickel, Fe, Co, Cu, and Zn, and them in consideration of the ease of the handling at the time of a spatter practical is suitable. In addition, aluminum, In, Sn, Pb, etc. are available. As a ceramic phase used as a residual phase, more than a kind chosen from borides, such as carbide, such as oxide, such as an alumina, a mullite, cordierite, a spinel, a zeolite, and forsterite, silicon carbide, titanium carbide, and zirconium carbide, titanium boride, zirconium boride, and boron carbide, can use suitably.

[0012] When forming the bipolar membrane of the above-mentioned metal and the ceramics by a spatter etc., on a metal target, the wafer of ceramic ingredients, such as a metallic oxide, metallic carbide, and a metal boride, can be placed, and it can use as a multicomponent target. Still more preferably, in order to make small dispersion in a presentation inside the film after membrane formation, the composite material mixed to homogeneity by the powder metallurgy-approach at the time of target production is prepared.

[0013] The substrate used in case the above porous-ceramics film is manufactured can be chosen from glass, the ceramics, plastics, and a heat-resistant metal, and can also use not a still more precise substrate but a porous substrate. As a heat-resistant metal used for a substrate, oxidation-resistant alloys, such as stainless steel which consists of Fe, nickel, Cr, V, etc., and Hastelloy, are suitable. Drawing 2 shows how to form membranes, using a porous-ceramics substrate as an example. That is, the front face is ground in the condition of having sunk a metal or resin into the front face of the ceramic porous body of dozens of micron meter from the several nm average aperture, and a smooth front face is formed. Subsequently, this front face is washed using water, a surfactant, an organic solvent, etc., and the spatter film is formed on it by making this into a substrate. At this time, it is desirable to use what is removed on the etching conditions same as the metal which sinks in, or resin as the ingredient of the above-mentioned metal target.

[0014] Next, with an acid or an alkali solution, etching processing is carried out and the metal component in the obtained bipolar membrane is removed. It is desirable to choose suitably according to the class of metal which can use a sulfuric acid, a hydrochloric acid, a nitric acid, oxalic acid, an acetic acid, etc., and should be carried out elution as an acid used by this etching processing. Since the ceramic part formed of the first membrane formation process has many amorphous or things which have low extent of crystallization, it is desirable to etch on weak etching conditions using the fully diluted solution. For example, Co is used as a metal component and it is SiO₂ as a ceramic component. When using, it is desirable to process with the etch rate of 0.3nm/s using the nitric-acid water solution of 0.003 conventions.

[0015] As stated above, in case the manufacture approach of the porous-ceramics film of this invention forms the porous-ceramics film, it produces the bipolar membrane of a metal and the ceramics by vapor growth, it is characterized by using combining the approach etching subsequently removes a metal phase, and can offer the various porous-ceramics film which has new structure and a new presentation. As for the porous-ceramics film of this invention, it is possible to make the isolation in nano meter size discover, and it is useful as a filter for separating a molecule and a particle etc. The porous-ceramics film of this invention can control independently the width of face of a pole diameter and a grain boundary phase (thicken width of face of a grain boundary phase especially), and essentially differs from the conventional anodic oxidation alumina film etc. at this point.

OPERATION

[Function] When the two phase from which the chemical durability which consists of a metal and ceramics (a metallic oxide, a metal boride, metallic carbide) differs by the forming-membranes methods, such as a spatter, in this invention forms the bipolar membrane intermingled with nanometer order, subsequently removes only a metal part by acid etching etc. and makes a ceramic part remain, it becomes possible to compound the porous-ceramics film which has single dimension penetration pore with little pressure loss. That is, by controlling membrane formation conditions appropriately, the metal phase which is one of the main membrane components is grown up in the shape of a column, a ceramic ingredient is deposited in the grain boundary, and it becomes possible by removing a metal phase by etching further to obtain the porous-ceramics film which has the single dimension penetration pore of the pole diameter of nanometer order.

[0017] Moreover, in order to form the bipolar membrane before carrying out acid etching by a spatter etc., it becomes available [the thing of a variety and various ingredients, such as a metal, glass, ceramics, and plastics, and a gestalt] at the substrate which supports the film.

EXAMPLE

[Example] An example explains this invention concretely below.

They are metals Co and SiO₂ on a soda lime glass substrate with an example 1 thickness of 1.2mm. The compound thin film which consists of two phases was formed. In a spatter, it is SiO₂ of 1cm angle on a metal Co target with a diameter of 6 inches. The

multicomponent target which placed the glass tip was used. At this time, it is SiO₂ so that 20% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10⁻⁶Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might serve as 2x10⁻²Torr, the RF of 600W was inputted, and the plasma was generated. The membrane formation rate at this time is about 1 nm/sec, and neither substrate heating nor impression of bias voltage was performed at the time of membrane formation.

[0019] The structure of the compound thin film which formed membranes is shown in the transmission electron microscope photograph of drawing 1. Drawing 1 is the enlargement which carried out grinding of the glass substrate, removed it, carried out ion polish of the bipolar membrane further, made thin, and was seen from the direction perpendicular to a film surface. With this photograph, Co crystal grain child with a mean particle diameter of 12nm is growing in the shape of a column, and it is SiO₂ amorphously to a grain boundary. It deposits.

[0020] Next, it was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of thickness produced by the above-mentioned approach for 5 minutes, and dissolution removal of the Co phase was carried out. Drawing 3 is the enlargement which observed the film after carrying out dissolution removal of this Co phase with the scanning electron microscope. Co phase is eluted nearly completely and it is SiO₂ of a grain boundary. It remained in the shape of a mesh. Expansion of the ceramic film obtained by drawing 4 by doing in this way and an example of a perspective view are shown.

[0021] By the same procedure as example 2 example 1, they are metals Co and SiO₂ on a soda lime glass substrate with a thickness of 1.2mm. The compound thin film which consists of two phases was formed. In a spatter, it is SiO₂ of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO₂ so that 10% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10⁻⁶Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10⁻²Torr, the RF of 600W was inputted, and the plasma was generated. The membrane formation rate at this time is about 1 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0022] Drawing 1 is resembled very well, the crystal grain child of Co grows in the shape of a column, and the structure of the compound thin film which formed membranes is SiO₂ amorphous to that grain boundary. It deposited and the mean particle diameter of Co crystal was large a little with about 20nm in this case. It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of this thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is SiO₂ of a grain boundary. It remained in the shape of a mesh.

[0023] By the same procedure as example 3 example 1, they are metals Co and SiO₂ on a soda lime glass substrate with a thickness of 1.2mm. The compound thin film which consists of two phases was formed. In a spatter, it is SiO₂ of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip

was used. At this time, it is SiO₂ so that 10% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10⁻⁶Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10⁻²Torr, the RF of 600W was inputted, and the plasma was generated. The membrane formation rate at this time is about 1 nm/sec, and heated the substrate at about 200 degrees C at the time of membrane formation.

[0024] Drawing 1 is resembled very well, Co crystal grain child grows in the shape of a column, and the structure of the compound thin film which formed membranes is SiO₂ amorphous to that grain boundary. It deposited and it turned out [about 35nm and] that the mean particle diameter of Co crystal is still larger in this case.

[0025] It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of this thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is SiO₂ of a grain boundary. It remained in the shape of a mesh.

[0026] By the same procedure as example 4 example 1, they are metals Co and SiO₂ on the Hastelloy substrate with a thickness of 2mm. The compound thin film which consists of two phases was formed. In a spatter, it is SiO₂ of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO₂ so that 10% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10⁻⁶Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10⁻²Torr, the RF of 600W was inputted, and the plasma was generated. The membrane formation rate at this time is about 1 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0027] It is very well alike in drawing 1 , Co crystal grain child grows in the shape of a column, and the structure of the compound thin film which formed membranes is SiO₂ amorphous to that grain boundary. It deposited and the mean particle diameter of Co crystal in this case was about 25nm.

[0028] It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of this thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is SiO₂ of a grain boundary. It remained in the shape of a mesh, and most exfoliations of the film from the Hastelloy substrate were not accepted.

[0029] In the same procedure as example 5 example 1, the compound thin film which consists of two phases of metals Co and SiO₂ was formed on the alumina substrate with a thickness of 5mm. In a spatter, it is SiO₂ of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO₂ so that 10% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10⁻⁶Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10⁻²Torr, the RF of 600W was inputted, and the plasma was generated. The membrane formation rate at this time is about 1 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0030] It is very well alike in drawing 1 , Co crystal grain child grows in the shape of a column, and the structure of the compound thin film which formed membranes is SiO₂ amorphous to the grain boundary. It deposited and the mean particle diameter of Co crystal was about 19nm.

[0031] It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of this thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is SiO₂ of a grain boundary. It remained in the shape of a mesh, and most exfoliations of the film from an alumina substrate were not accepted.

[0032] By the same procedure as example 6 example 1, they are metals Co and SiO₂ on a polyethylene film substrate with a thickness of 0.8mm. The compound thin film which consists of two phases was formed. In a spatter, it is SiO₂ of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO₂ so that 10% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10⁻⁶Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10⁻²Torr, the RF of 600W was inputted, and the plasma was generated. The membrane formation rates at this time are about 0.8 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0033] It is very well alike in drawing 1 , Co crystal grain child grows in the shape of a column, and the structure of the compound thin film which formed membranes is SiO₂ amorphous to the grain boundary. It deposited and the mean particle diameter of Co crystal was about 26nm.

[0034] It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is SiO₂ of a grain boundary. It remained in the shape of a mesh. When a polyethylene film was used as a substrate, exfoliation of the film took place quite notably in process of the etching processing by the acid. However, when the front face of a polyethylene film was processed by corona discharge treatment or the silane coupling agent before forming bipolar membrane by the spatter, it turned out that exfoliation is pressed down considerably.

[0035] The metal Co with a thickness of 100nm was formed on the porosity silica substrate with a thickness of 2mm by example 7 spatter. The front face of the substrate after membrane formation was ground with diamond polish equipment, it left Co got blocked in the pore of a silica, Co phase on a substrate was removed, and the smooth polished surface was acquired. They are metals Co and SiO₂ on this substrate. The compound thin film which consists of two phases was formed. In a spatter, it is SiO₂ of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO₂ so that 10% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10⁻⁶Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10⁻²Torr, the RF of 600W was inputted, and the plasma was generated. Membrane formation rates are about 0.8 nm/sec, and neither heating of a substrate nor impression of

bias voltage was performed at the time of membrane formation.

[0036] It is very well alike in drawing 1 , Co crystal grain child grows in the shape of a column, and the structure of the thin film which formed membranes is SiO₂ amorphous to the grain boundary. It deposited and the mean particle diameter of Co crystal was about 26nm.

[0037] Co phase which was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of this thickness for 5 minutes, and was got blocked in the pore of a silica, and Co-SiO₂ formed on it Dissolution removal of the Co phase in bipolar membrane was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is SiO₂ of a grain boundary. It is ***** to be removed nearly completely [Co phase which remained in the shape of a mesh and was got blocked in the pore of a porosity silica substrate]. Moreover, most exfoliations of the bipolar membrane from a porosity silica substrate were not accepted.

[0038] In the same procedure as example 8 example 1, the compound thin film which consists of two phases of Metals Co and SiC was formed on the soda lime glass substrate with a thickness of 1.2mm. The multicomponent target which placed the SiC sintered compact tip of 1cm angle on the metal Co target with a diameter of 6 inches was used for the spatter. At this time, the amount of a SiC sintered compact chip was adjusted so that 20% of the total surface area of one side of a target might be occupied. After exhausting a vacuum tub to 5x10⁻⁶Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10⁻²Torr, the RF of 600W was inputted, and the plasma was generated. Membrane formation rates are about 0.9 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0039] The structure of the compound thin film which formed membranes was very well alike in drawing 1 , Co crystal grain child grew in the shape of a column, and the phase considered to be amorphous SiC by the grain boundary deposited. This Co crystal grain child's mean particle diameter was about 35nm.

[0040] It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase was eluted nearly completely and SiC of a grain boundary remained in the shape of a mesh.

[0041] By the same procedure as example 9 example 1, they are metals Co and ZrB₂ on a soda lime glass substrate with a thickness of 1.2mm. The compound thin film which consists of two phases was formed. In a spatter, it is ZrB₂ of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the ceramic tip was used. At this time, it is ZrB₂ so that 20% of the total surface area of one side of a target may be occupied. The amount of a ceramic chip was adjusted. After exhausting a vacuum tub to 5x10⁻⁶Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10⁻²Torr, the RF of 600W was inputted, and the plasma was generated. Membrane formation rates are about 0.9 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0042] It is very well alike in drawing 1 , Co crystal grain child grows in the shape of a column, and the structure of the compound thin film which formed membranes is ZrB₂ amorphous to that grain boundary. It deposited and this Co crystal grain child's mean

particle diameter was about 21nm.

[0043] It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is ZrB₂ of a grain boundary. It remained in the shape of a mesh, and most exfoliations of the film from a soda lime glass substrate were not accepted.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Co-SiO₂ Enlargement which observed the system prototype sample from the direction perpendicular to a film surface with the transmission electron microscope.

[Drawing 2] The schematic diagram of the procedure which forms the porous-ceramics film of this invention on a porous-ceramics substrate.

[Drawing 3] It sets to this invention and is Co-SiO₂ on a soda lime glass substrate. Scanning electron microscope photograph which looked at what was etched with the nitric acid of 0.003 conventions after creating bipolar membrane by the spatter from [membranous] the cross section.

[Drawing 4] The perspective view showing the outline of the porous-ceramics film by this invention.

[Description of Notations]

- (a) The sectional view of a porous-ceramics substrate
- (b) The situation in which the metal membrane was formed on the ceramic substrate (the pore on the front face of a substrate is filled up with a metal)
- (c) The condition which ground the front face until the ceramic substrate front face appeared
- (d) The condition in which the metal and ceramic bipolar membrane of this invention were formed on the film obtained by (c)
- (e) The condition after a metal is eluted by etching by the acid

drawings attached to email

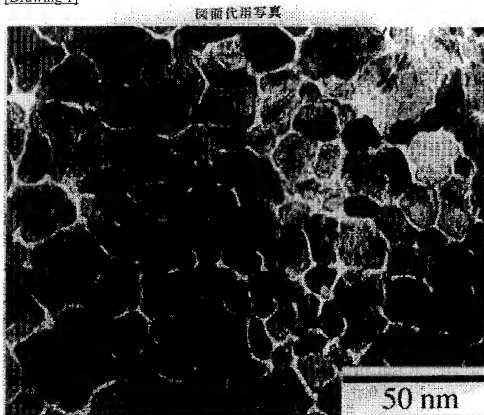
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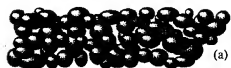
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DRAWINGS

[Drawing 1]



[Drawing 2]

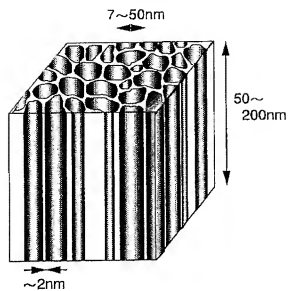


[Drawing 3]

図面代用写真



[Drawing 4]



[Translation done.]